

Subject: Chains, Rings and Spectroscopy **Code:** 2814

Session: June **Year:** 2004

Final Mark Scheme

MAXIMUM MARK	90
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ADVICE TO EXAMINERS ON THE ANNOTATION OF SCRIPTS

1. Please ensure that you use the **final** version of the Mark Scheme.
You are advised to destroy all draft versions.
2. Please mark all post-standardisation scripts in red ink. A tick (✓) should be used for each answer judged worthy of a mark. Ticks should be placed as close as possible to the point in the answer where the mark has been awarded. The number of ticks should be the same as the number of marks awarded. If two (or more) responses are required for one mark, use only one tick. Half marks should never be used.
3. The following annotations may be used in when marking. No comments should be written on scripts unless they relate directly to the mark scheme. Remember that scripts may be returned to centres.

x	=	incorrect response (errors may also be underlined)
^	=	omission of the correct response
<i>bod</i>	=	“benefit of the doubt” (where professional judgement has been used in deciding a response is worthy of a mark)
<i>ecf</i>	=	“error carried forward” (in consequential marking)
<i>con</i>	=	contradiction (in cases where candidates contradict themselves in the same response). No mark awarded, even if one response was correct. ¹
<i>sf</i>	=	error in the number of significant figures (only penalised once on the paper).

4. The marks awarded for each part question should be indicated in the margin provided on the right hand side of the page. The mark total for each question should be ringed at the end of the question, on the right hand side. These totals should be added up to give the final total on the front of the paper.
5. In cases where candidates are required to give a specific number of answers, (e.g. ‘give three reasons ...’), mark the first answer(s) given up to the total number required. Strike through the remainder. In specific cases where this rule cannot be applied, the exact procedure to be used is given in the mark scheme
6. Correct answers to calculations should gain full credit even if no working is shown, unless otherwise indicated on the mark scheme. (An instruction to ‘Show your working’ is to help candidates, who may then gain partial credit even if their final answer is not correct.)
7. Strike through all blank spaces and/or pages in order to give clear indication that the whole of the script has been considered.
8. An element of professional judgement is required in the marking of any written paper, and candidates may not use the exact words that appear in the mark scheme. If the science is correct and answers the question, then the mark(s) should normally be credited. If you are in doubt about the validity of any answer, contact your Team Leader/Principal Examiner for guidance.

¹ Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

**Abbreviations,
annotations and
conventions used in the
mark scheme**

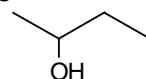
/ = alternative and acceptable answers for the same marking point
; = separates marking points
NOT = answers not worthy of credit
= words which are not essential to gain credit
() (underlining) = key words which must be used
— = allow error carried forward in consequential marking
ecf = alternative wording
AW = or reverse argument
ora

**Marking structures in
organic chemistry**

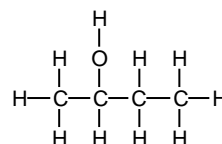
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH₃, C₂H₅, OH, COOH, COOCH₃) to unambiguously define the arrangement of the atoms. (E.g. C₃H₇ would not be sufficient).

If not specified by the question, this may be given as either:

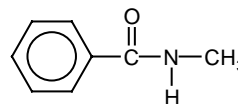
- a **structural formula** – e.g. CH₃CH(OH)C₂H₅,



- a **skeletal formula** – e.g. ,



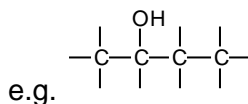
- a **displayed formula** – e.g.



or as a hybrid of these – e.g.

The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –



Benzene rings may be represented as



as well as



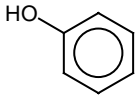
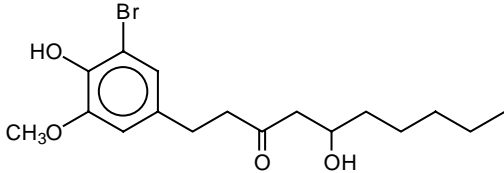
in any

of the types of formula above.

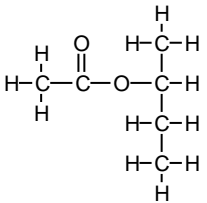
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Qu.	Expected answers:	Alternative responses:	Marks:
1 (a) (i)	carboxylic acid ✓	NOT 'carboxyl'	[1]
(ii)	$\text{CH}_3\text{CH}(\text{NH}_2)\text{COO}^- \text{Na}^+$ or a displayed structure where ... $\text{COO}^- / \text{COONa}$ ✓ rest of the structure including Na also correct ✓	allow 1 overall for covalent O-Na or missing charge on COO but otherwise correct	[2]
(iii)	water / H_2O ✓		[1]
(b)	H_3N^+ becomes H_2N ✓ rest of the ion unchanged ✓		[2]
(c)	condensation / water molecule removed / created (or shown) ✓ NH_2 (from one molecule) reacts with the COOH (from the other molecule) (or shown by drawing around the groups) ✓ AW $\begin{array}{c} \text{H} \\ \\ \text{—C—N—} \\ \\ \text{O} \end{array}$ displayed at least once ✓ one correct dipeptide structure - eg $\begin{array}{ccccccc} & \text{CH}_3 & & \text{H} & & \text{C}_3\text{H}_7 & \\ & & & & & & \\ \text{H}_2\text{N} & -\text{C} & - & \text{C} & - & \text{N} & - & \text{C} & - & \text{COOH} \\ & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & \end{array}$ ✓ second correct dipeptide structure – eg $\begin{array}{ccccccc} & \text{C}_3\text{H}_7 & & \text{H} & & \text{CH}_3 & \\ & & & & & & \\ \text{H}_2\text{N} & -\text{C} & - & \text{C} & - & \text{N} & - & \text{C} & - & \text{COOH} \\ & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & \end{array}$ / or <i>ecf</i> which clearly shows the idea of amino acids swapping ✓	allow any correct displayed isomer of C_3H_7 allow ALA-ALA and VAL-VAL allow -CONH- on the dipeptides	[5]
			[Total: 11]

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Qu.	Expected answers:	Alternative responses:	Marks:
2 (a)	A phenol ✓ C (secondary) alcohol ✓	NOT 'hydroxyl' for A or C	[3]
(b) (i)	B / ketone / carbonyl ✓		[1]
(ii)	yellow/orange/red ✓ precipitate/crystals/solid ✓		[2]
(iii)	(gingerol would not react because) ... it does not contain an aldehyde group / only aldehydes can react with Tollens' Reagent / only aldehydes can be easily oxidised / ketones cannot be oxidised further ✓	NOT just "ketones don't react" etc	[1]
(c)	 / phenol / A	do not penalise the CH ₃ O- if included	[1]
(d) (i)	bromination of the benzene ring ✓ eg  other functional groups also unaffected ✓	allow mono, di or tri-bromination at any position	[2]
(ii)	HBr / hydrogen bromide		[1]
(e)	peak at 3400cm ⁻¹ labelled O-H ✓ peak at 1700cm ⁻¹ labelled C=O ✓	if more than two peaks labelled, mark the incorrect peaks first	[2]
(f) (i)	same structural/displayed formula / same order of bonds ✓ different spatial /3-d arrangement ✓		[2]
(ii)	optical (isomerism) ✓		[1]
[Total: 16]			

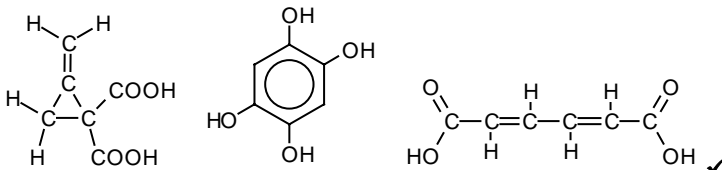
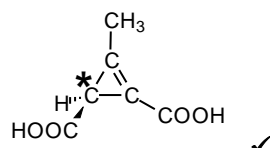
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Qu.	Expected answers:	Alternative responses:	Marks:
3 (a) (i)	(conc) H ₂ SO ₄	NOT just H ⁺ / acid or anything suggesting the acid is dilute	[1]
(ii)	to prevent loss (of reactants/products) by evaporation / vapours AW		[1]
(b) (i)	 <p>correct displayed ester group: $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{O}-\text{C} \end{array}$ ✓</p> <p>rest of the structure also correct ✓</p>		[2]
(ii)	butan-2-ol ✓	NOT just butanol	[1]
(c)	flavouring / perfume	NOT any solvent type uses such as nail-varnish nor medicines etc	[1]
[Total: 6]			

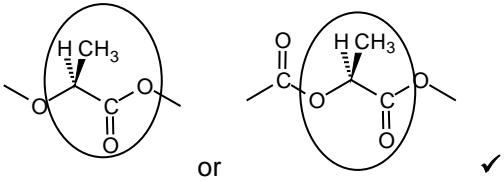
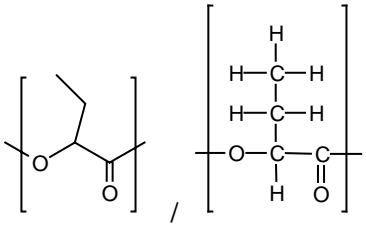
4 (a)	<p>% O = 45.1 ✓</p> <p>C = 50.7/12.0 = 4.2 4.225 / 2.819 = 1.499 ≈ 1.5 = 3</p> <p>H = 4.2 / 1.0 = 4.2 4.2 / 2.819 = 1.490 ≈ 1.5 = 3</p> <p>O = 45.1 / 16.0 = 2.8 (or ecf) 2.819 / 2.819 = 1.000 = 1.0 = 2</p> <p>calculation of moles ✓</p> <p>C₃H₃O₂ clearly deduced from the ratio of moles ✓</p>	<p>NOT any method which works back from the molecular formula</p>	[3]
(b) (i)	<p>empirical formula has M_r = 36 + 3 + 32 = 71 (or ecf) ✓</p> <p>2 x empirical M_r = 142 / within range 138-144 ✓</p>	<p>only allow ecf on 2nd mark if 2 x M_r is still 138-144</p>	[2]
(ii)	mass spectrometry ✓		[1]

Question 4 continues overleaf

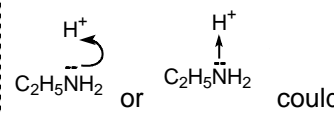
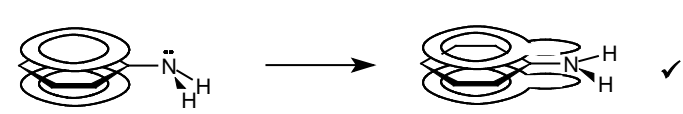
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Qu.	Expected answers:	Alternative responses:	Marks:
4 (c)	any valid structure eg 		[1]
(d) (i)	carbon with 4 different groups attached ✓	allow "functional groups"	[1]
(ii)			[1]
(e) (i)	carboxylic acid / COOH (protons)	NOT just "OH protons"	[1]
(ii)	D replaces protons on OH groups / OH protons are labile ✓ peak for (CO)OH protons disappears ✓		[2]
(iii)	(E is the correct structure because ...) peaks Y and Z are due to two (equivalent) protons ✓ EITHER comparing peak areas ... structure E has groups: =CH ₂ / two CH ✓ structure F would give a peak with area 3/area 1 ✓ OR comparing the number of peaks ... structure E has three environments/ H _a , H _b , H _c are labelled on the structure ✓ structure F would give four peaks (inc. COOH) ✓	ignore which groups are assigned to peaks Y and Z ignore any reference to shift values, -CO-CH ₂ -R, or (lack of) splitting	[3]
			[Total: 15]

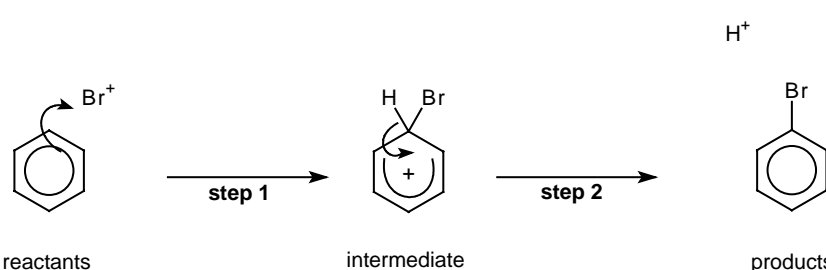
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Qu.	Expected answers:	Alternative responses:	Marks:
5 (a)	<p>stage 1</p> <p>HCN ✓ KCN ✓ nucleophilic addition ✓</p> <p>$\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$ ✓</p> <p>stage 2</p> <p>(named) dilute acid / $\text{H}^+(\text{aq})$ ✓ heat/reflux ✓ hydrolysis ✓</p> <p>$\text{CH}_3\text{CH}(\text{OH})\text{CN} + 2\text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH} + \text{NH}_3$ or including H^+ on the left to give NH_4^+ ✓</p>	<p>allow KCN with $\text{HCl}/\text{H}_2\text{SO}_4$ or HCN with NaOH for the first two marks, but acid/alkali does not score on its own.</p> <p>reagents and conditions can be on either line</p>	[8]
(b) (i)	condensation ✓		[1]
(ii)			[1]
(iii)	<p>(fermentation because ...)</p> <p>natural processes (often) produce one (optical) isomer ✓ synthetically gives a mixture of (both optical) isomers ✓</p>	allow "racemic"	[2]
(c) (i)	poly(propene) / poly(phenylethene) ✓	must be a hydrocarbon allow new or old names	[1]
(ii)	<p>atactic ✓ syndiotactic ✓</p>		[2]
(d)	<p>a correct repeat of a polyester with 'sticks'/bracketed ... with the ester bond displayed/skeletal ✓</p> <p>side chain/hydrogens also correct and the repeat shows only one monomer ✓</p> 	Do NOT allow H or OH at either end if no brackets	[2]
			[Total: 17]

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
Qu.	Expected answers:	Alternative responses:	Marks:
6 (a)	<p>ethylamine/bases react with/accept a proton/H^+ ✓</p> <p>to give $C_2H_5NH_3^+$ ✓</p> <p>(using the) lone pair of electrons on the N atom of the amine / lone pair is shown on the N of a correct structure of the amine ✓</p> <p>a dative covalent bond forms between N and H / curly arrow shown from lone pair towards H^+ / dative bond shown from N to H ✓</p>	<p>must be stated somewhere</p> <p>  $C_2H_5NH_2$ or $C_2H_5NH_2$ could score the last two marks </p>	[4]
(b)	<p>(phenylamine is a weaker base because ...)</p> <p>the phenyl group pulls electrons away from the nitrogen ✓</p> <p>the lone pair is delocalised / interacts with the π electrons over the ring / or shown in a suitable diagram – eg</p> <p>  </p> <p>the lone pair is not donated as easily / is less available / H^+ is not accepted as easily ✓</p>	<p>must be clear which way electrons are going</p>	[3]
			[Total: 7]

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Qu.	Expected answers:	Alternative responses:	Marks:
7 (a) (i)	iron / iron(III)bromide / aluminium chloride etc ✓	accept any iron(III) or aluminium chloride/bromide but NOT just "iron bromide"	[1]
(ii)	halogen carrier ✓	accept Lewis acid but NOT "Friedel-Crafts catalyst"	[1]
(iii)	$\text{C}_6\text{H}_6 + \text{Br}_2 \longrightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$ HBr as product ✓ rest of the equation also correct ✓	allow H^+ and Br^- allow a balanced equation for di or tri bromination	[2]
(iv)	bromobenzene	allow name from di or tribromination in (iii) as long as they are correct	[1]
(b)	 <p>reactants intermediate products</p> <p>curly arrow from benzene π-bond to Br^+ ✓</p> <p>correct intermediate ✓ curly arrow from C-H bond to gap in π-bond ✓</p> <p>H^+ and bromobenzene as products ✓</p>	check curly arrows clearly start and finish at the correct atom / bond the 'smile' must reach round all 5 carbons with the + clearly not on the tetrahedral carbon	[4]

Question 7 continues overleaf

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Qu.	Expected answers:	Alternative responses:	Marks:
7 (c) (i)	<p>p-orbitals overlapping above and below the ring stated in words or shown in either diagram ✓</p> <p>correct diagrams of π-bonds in cyclohexene and benzene:</p> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <p style="text-align: center;">✓ ✓</p> <p><u>π-bond(s)/electrons</u> are labelled in either diagram or their position is described in words ✓</p> <p style="text-align: right;">4 marks on π-bonding</p>	<p>do NOT give the diagram mark if a double bond is also shown</p> <p>allow any reasonable attempt at the benzene π-bonds, but not a simple </p>	
(ii)	<p>the negative charge/π electrons are more spread out / delocalised (in benzene ora) ✓</p> <p>the bromine is less polarised / a catalyst is needed to polarise bromine (in benzene ora) ✓</p> <p>electrophiles / bromine are less attracted (to benzene ora) ✓</p> <p>more energy is needed (to break the π-bond) due to the delocalisation (in benzene ora) ✓</p> <p style="text-align: right;">AW</p> <p>ANY 3 out of 4 marks explaining different the reactivity</p> <p>Quality of Written Communication</p> <p>one mark for the correct use and organisation of both the following terms: p-orbitals, delocalised ✓</p> <p>one mark for correct spelling, punctuation and grammar in at least two sentences ✓</p>	<p>these marks can be gained from the explanation of the relative reactivity of either benzene or cyclohexene but a comparison must be made for each mark</p> <p>do NOT give the last mark for just saying that benzene is more stable than cyclohexene</p>	<p style="text-align: right;">[4]</p> <p style="text-align: right;">max [3]</p> <p style="text-align: right;">[2]</p> <p style="text-align: right;">[Total: 18]</p>